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## **Effective Medium Theory of DNA-linked Gold Nanoparticle Aggregates: Effect of Aggregate Shape**

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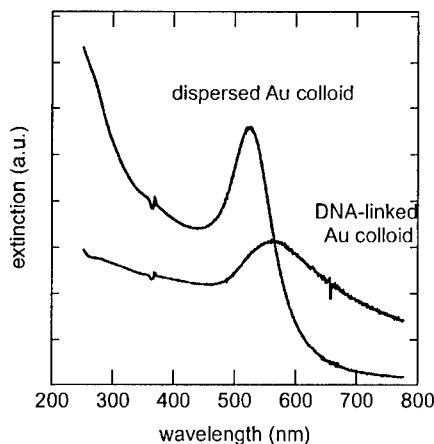
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### **ABSTRACT**

We present a dynamical effective medium theory (EMT) of the dielectric properties of nanoparticle aggregates formed from DNA-linked gold nanoparticles. Experimental measurements show that such aggregates have reduced UV extinction and plasmon bands that are considerably red-shifted and broadened relative to the plasmon absorption feature observed in spectra of dispersed colloid. The EMT, which can be used to reproduce the observed spectral changes, is tested by comparing aggregate spectra calculated using the EMT dielectric function with spectra from explicit coupled particle calculations, and good agreement is found. The EMT dielectric function is used as well in discrete dipole calculations to calculate extinction spectra for a variety of aggregate shapes not amenable to analytic solution, and the sensitivity of the spectra to aggregate shape is examined. We find that the spectra are only weakly sensitive to aggregate shape, and conclude that, when calculating extinction of the DNA-linked aggregates for comparison with experiment, spherical shapes can be assumed.

### **INTRODUCTION**

Recently, a DNA detection method has been developed that is based upon the distance-dependent optical properties of gold nanoparticle aggregates that form in the presence of DNA linker molecules.<sup>1-4</sup> Gold particles are functionalized with alkane-thiol-capped oligonucleotides (single-stranded DNA); complementary linker oligonucleotide (DNA) strands direct the assembly of nanoparticle networks through the forces of sequence-specific hybridization (DNA duplex formation). The optical properties of the linked nanoparticles have been shown to be a function of the size of the nanoparticles, the length of the linking duplex DNA, and the size of the nanoparticle aggregates. When nanoparticles of a size between 12 and 16 nm are linked with DNA duplexes composed of 24 oligonucleotide base pairs, aggregate formation is accompanied by a color change from red to purplish-blue (Figure 1).



**Figure 1.** Extinction spectra for dispersed and DNA-linked Au nanoparticles, courtesy of the authors of ref. 3. The 13 nm particles are capped with 3'- and 5'-(alkanethiol) 12-base oligonucleotides. The aggregated colloid is formed in the presence of a 24-base oligonucleotide, each half of which is complementary to the one of the two nanoparticle-capping oligonucleotides.

In earlier work, two of us demonstrated that aggregates composed of thousands of particles may be described accurately using a coupled dipole approach in which the particles are located on a cubic lattice, and the induced polarizations are determined using complex conjugate gradient solutions of the dipole interaction equations, with Fourier methods used to evaluate dipole-dipole interactions.<sup>5,6</sup> The dipole polarizability of each particle is determined exactly using Mie theory. Since the lattice does not represent a solid object, lattice sites may be unoccupied. This does not cause trouble with evaluating the dipole sums by Fourier transforms, but the method is restricted to aggregates wherein the particles are located on cubic lattices (sc, bcc, fcc or lattice gases). We find the lattice representation of the aggregates to be quite effective for the DNA/gold aggregates. We have tested this coupled dipole theory against more complete theories that include converged multipole expansions, and we find that, for the particle sizes and interparticle spacings that are characteristic of the DNA-linked nanoparticle aggregates, the coupled dipole results are accurate.

Another approach to describing the optical properties of nonmagnetic nanoparticle aggregates is to derive a dielectric function that characterizes the electric susceptibility of bulk aggregate. This effective medium approach takes advantage of the fact that optical wavelengths are much larger than either the particle size or the mean distance between particles. In this circumstance, a homogeneous description may provide an accurate representation of the heterogeneous material. In this paper we examine the properties of a recently developed dynamical effective medium theory (EMT) that was designed to treat aggregate structures similar to the DNA-linked nanoparticle aggregates.<sup>7,8</sup> These aggregates are typically hundreds of nanometers or microns in size and are composed of nanoparticles of a size between 10 and 30 nm. Typically, the metal fraction of the aggregates is less than 20% by volume. We will show by comparison with coupled dipole theory that the low volume fractions and small nanoparticle sizes make it relatively easy to develop an EMT that is accurate. However, because the

aggregate sizes are comparable to the wavelength of light, extinction spectra are difficult to determine unless the aggregates are spherical. Nonspherical aggregates, however, can be treated using a finite element based approach, the discrete dipole approximation (DDA),<sup>9</sup> with the EMT dielectric function as input. We present DDA results for a variety of nonspherical aggregates and compare them with spectra calculated for spherical aggregates to determine the sensitivity of aggregate extinction to aggregate shape.

## THEORY

The simplest approach to constructing an EMT is to assume that the particles are non-interacting. Under this assumption, the polarization of a small spherical aggregate can be evaluated by summing the response of all the spheres of which an aggregate is composed. For each sphere, the polarizability (in the long wavelength limit) is

$$\alpha_o = \frac{\epsilon - 1}{\epsilon + 2} a^3$$

where  $a$  is the sphere radius and  $\epsilon$  is the metal dielectric function. The polarizability of a small sphere of aggregate material of radius  $R$  ( $R \ll \lambda$ ) is given by a similar expression:

$$\alpha_{agg} = \frac{\epsilon_{eff} - 1}{\epsilon_{eff} + 2} R^3$$

where the effective aggregate dielectric function is  $\epsilon_{eff}$ . Alternatively, invoking the additivity that follows from the assumption of a non-interacting response,  $\alpha_{agg} = N\alpha_o$ , where  $N$  is the number of spheres in the sphere of aggregate material. Substituting the expressions above, we obtain the following relation between  $\epsilon$  and  $\epsilon_{eff}$ :

$$\frac{\epsilon_{eff} - 1}{\epsilon_{eff} + 2} = f \frac{\epsilon - 1}{\epsilon + 2}$$

where  $f$  is the volume fraction of metal spheres ( $f = Na^3/R^3$ ). This formula defines the well known Maxwell-Garnett effective medium dielectric constant, and it is actually much better than this trivial derivation would imply. However, it does not describe electrodynamic effects.

To describe electrodynamic effects, we use a result from a theory of Draine and Goodman<sup>9</sup> that is at the heart of their important improvement to the DDA method. Draine and Goodman demonstrated that the optical response of a lattice of dipoles can be made to match that of bulk continuum by an appropriate choice of the wavevector-dependent dipole polarizability,  $\alpha$ , provided that the lattice parameter is sufficiently small. The expression that relates the polarizability to the bulk dielectric function is referred to as the "lattice dispersion relationship". In our approach,<sup>7</sup> the relationship is inverted (at each wavelength) to determine the value of the dielectric function,  $\epsilon_{eff}$ , from the known nanosphere polarizability. The relevant formula is:

$$\alpha = \frac{\alpha_o}{1 + \frac{\alpha_o}{d^3} \frac{3}{4\pi} \left[ (b_1 + \epsilon_{\text{eff}} b_2 + \epsilon_{\text{eff}} b_3 S)(kd) - \frac{2}{3} i(kd)^3 \right]}$$

where

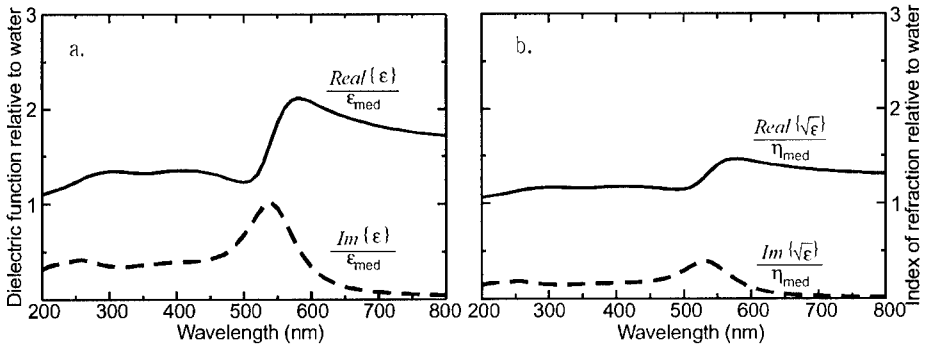
$$\alpha_o = \frac{\epsilon_{\text{eff}} - 1}{\epsilon_{\text{eff}} + 2} a^3$$

In this expression,  $d$  is the lattice spacing,  $k$  is the magnitude of the wavevector,  $b_1, b_2$ , and  $b_3$  are constants, and  $S$  is a geometric factor that depends on the direction of the wavevector relative to that of the lattice. In our implementation of the lattice dispersion relationship,  $\alpha$  is the exact nanosphere dipole polarizability as obtained from Mie theory. Further details, along with comparisons between Maxwell-Garnett theory and the new dynamical effective medium approximation are given in Ref. 7. In the next section, we demonstrate the accuracy of the theory and use it to examine the sensitivity of aggregate UV-vis extinction spectra to aggregate shape.

## RESULTS

### A. EMT Dielectric Functions

The dielectric function for a material composed of 13 nm Au spheres in water is illustrated in Fig. 2a, for frequencies that correspond to UV and visible radiation. The metal fraction,  $f$ , of the nanoparticle material is 0.155 by volume, which is the inclusion fraction of a simple cubic array of spheres separated by a distance equal to a particle radius,  $r$ , i.e. an sc lattice with lattice parameter equal to  $1.5r$ . The function is complex, indicating that the material is absorptive as well as refractive. The index of refraction (square root of the dielectric function) is illustrated in Fig. 2b.

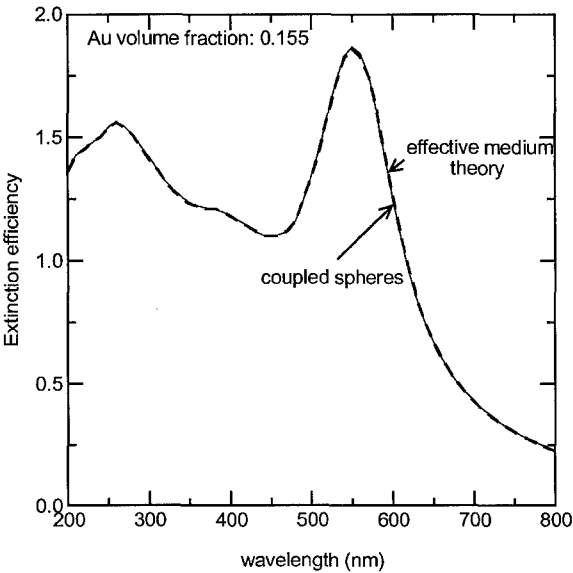


**Figure 2.** (a) Complex dielectric function,  $\epsilon$ , and (b) complex index of refraction,  $\eta$ , for a material composed of 13 nm Au nanoparticles (metal fraction 0.155) in water. The effective dielectric function and index of refraction are shown relative to  $\epsilon$  and  $\eta$  of the medium, 1.77 and 1.33 respectively.

The peak absorption of the nanoparticle material occurs at the frequency at which the imaginary part of the index of refraction is a maximum, which, for this material, is at a wavelength of 532 nm. From the real part of the index it can be seen that the material refracts light primarily at frequencies lower than that of peak absorption, i.e. at wavelengths corresponding to red or IR light.

**B. Optical Response of a Nanoparticle Aggregate: Comparison with Coupled-Dipole Results**

At each frequency for which the dielectric properties of a material are known, an electrodynamic problem can be posed for a given sample size and shape whose solution yields the extinction of that sample. Using the nanoparticle dielectric function described above, we have calculated the extinction spectrum of a spherical aggregate of 13 nm Au nanoparticles in water that is 234 nm in diameter. We have chosen an aggregate that is spherical in shape so that the calculation is a simple application of Mie theory, a rigorous theory for spherical objects. To test the accuracy of our dielectric function, we perform another more involved calculation that treats the heterogeneity of the nanoparticle material directly and models each of the 912 particles explicitly. We use a level of theory (coupled dipole theory) that we have tested against higher order theories<sup>5</sup> and have shown to be accurate for nanoparticles of this size that are separated by distances greater than or equal to a nanoparticle radius, as is the case here. Extinction spectra calculated by the two methods are shown together for comparison in Figure 3. Extinction is



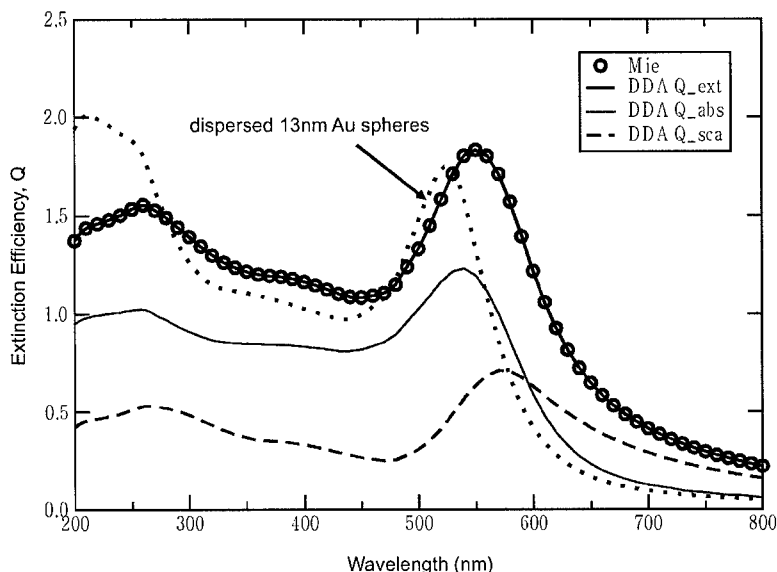
**Figure 3.** Extinction spectra of a 234 nm spherical aggregate of 13 nm spheres in water, arranged on a simple cubic lattice. The aggregate is 15.5% Au by volume. The solid line is the extinction as calculated with each nanoparticle modeled explicitly; the dashed line is extinction as calculated with Mie theory using the effective dielectric function of the nanoparticle material as input.

plotted as an efficiency, i.e. the extinction cross section relative to the geometric cross section. The perfect agreement of the two results validates the use of a homogeneous description of the nanoparticle material and, in particular, the dynamical effective medium theory.

### C. DDA Method for Calculating Extinction Spectra

Having demonstrated the ability of our dielectric function to accurately represent nanoparticle material dielectric response, we seek to use it to predict optical spectra of aggregates that are not spherical and, therefore, not addressable with Mie theory. To accomplish this, we adopt a method of solution known as the Discrete Dipole Approximation<sup>9</sup> (DDA) that is most widely applied to solid scatterers. The DDA approach involves a discretization of the interior of the scatterer (or 'target') into a lattice of polarizable dipoles, whose polarizabilities are derived from the dielectric function of the target material. The approach is fully flexible with respect to aggregate shape. The method is described in detail in Ref. 9, and a previous application is presented in Ref. 10. Because of the dielectric nature of the nanoparticle material, the lattice spacing of the DDA grid that discretizes the aggregate interior can be quite large relative to that required to obtain converged results when applying the method to a metallic target. Note that, for these calculations, the grid used for computation is unrelated to the actual spacing between nanoparticles.

To test the DDA approach, we use the method first to calculate the extinction spectrum of an aggregate whose dielectric function and spectrum are known. In Figure 4 we display the DDA result for our 234 nm spherical aggregate of 13 nm Au spheres in water (0.155 Au by volume) and compare it to the extinction spectrum computed previously using Mie theory. In both cases, our derived nanomaterial dielectric function, illustrated in Fig. 2a, is used as input. From the nearly exact match of the two spectra, we conclude that the discrete dipole approximation is accurate for materials of this type and can be used with confidence to calculate spectra for arbitrarily shaped aggregates, as desired. Also shown in Fig. 4 are contributions to the extinction spectrum from absorption and scattering and, for comparison with the aggregate spectrum, a spectrum of dispersed ( $f = 0.155 \times 10^{-3}$ ) 13 nm Au spheres. (The dispersed particle extinction has been scaled by a factor of 100 to compensate for the larger size of the geometric cross section used to normalize the extinction cross section when calculating efficiencies,  $Q_{\text{ext}} = C_{\text{ext}}/C_{\text{geom}}$ , for the dispersed case relative to  $C_{\text{geom}}$  of the aggregate.) Clearly, both the absorption and scattering maxima are red shifted from the absorption maximum of the dispersed spheres. (The dispersed 13 nm particles are too small to scatter visible light; hence, their extinction spectrum is essentially an absorption spectrum.) The aggregate absorption maximum occurs at approximately the same wavelength as the maximum in the imaginary part of the nanoparticle material index of refraction (Fig. 2b). Scattering occurs primarily at longer wavelengths, as expected given the nonrefractive nature of the material at shorter wavelengths. While larger aggregates would scatter light at longer wavelengths as well, significant scattering for these smaller aggregates is limited to wavelengths less than 700 nm, consistent with the notion that the phase variation,  $kD$ , across a target of size  $D$  must be greater than 1 for significant scattering to occur.

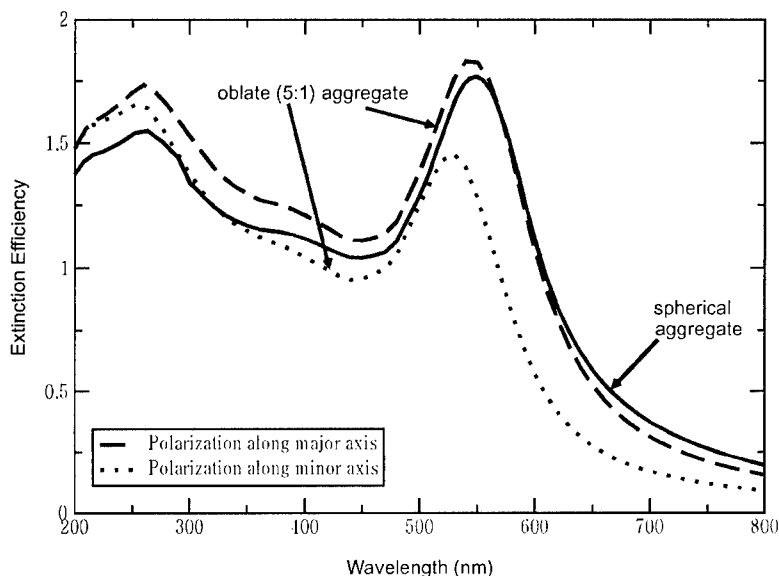


**Figure 4.** Extinction spectra of the 234 nm DNA-linked gold aggregate (metal fraction 0.155) in water: comparison of spectrum calculated using the Discrete Dipole Approximation and spectrum (from Fig. 3) calculated using Mie theory. The similarity of the two spectra validates the use of the DDA in subsequent calculations. The spectrum of dispersed 13 nm Au particles (of which the aggregate is composed) in water is shown as well, as are the absorption and scattering contributions to the aggregate extinction.

#### D. EMT Spectra of Nonspherical Aggregates

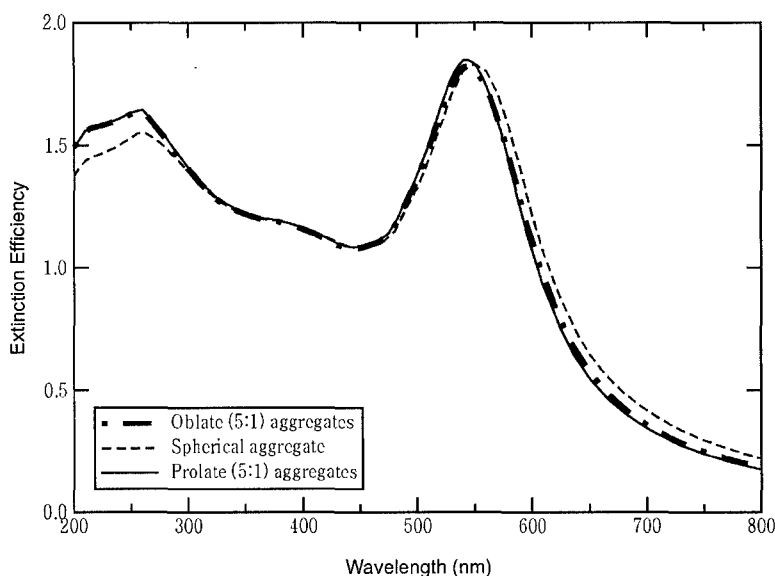
The DDA method was used to calculate spectra of other aggregates of 13 nm Au particles (Au fraction 0.155) from the same dielectric function. Spectra of a 5:1 oblate aggregate equal in volume to a spherical aggregate of diameter 234 nm are illustrated in Figure 5. The spectra depend upon the orientation of the polarization and propagation axes of the incident light relative to the principle axes of the ellipsoidal aggregate. Two spectra are shown, one for polarization along one of the major axes of the aggregate and one for polarization along the minor axis. In both cases, the propagation direction is along a major axis. Both spectra display peaks at wavelengths significantly shorter than that of the spectrum of a spherical aggregate; for the case of polarization along the minor axis, the spectrum has a plasmon peak that is closer to that of dispersed Au colloid than to a spherical aggregate of the same volume. In the UV, however, all spectra are quite similar, indicating insensitivity of the extinction in this wavelength region to aggregate shape. Similar calculations were done for 5:1 prolate ellipsoids of equal volume. In the visible, these spectra are closer to that of a spherical aggregate than are the spectra of oblate ellipsoidal aggregates, and in the UV, they are again similar.





**Figure 5.** Extinction spectra of DNA-linked gold nanoparticle aggregates: comparison of a 234 nm spherical aggregate and an equivolume 5:1 oblate aggregate. In the UV, the spectra are similar. In the visible, when the polarization direction is aligned relative to the aggregate, spectra are polarization- and aggregate shape-dependent.

Since, in solution, where the DNA-linking takes place and the aggregate spectra are collected, aggregates assume random orientations relative to a light source, we calculated as well orientationally-averaged extinction spectra for both oblate and prolate (5:1) aggregates of 13 nm Au spheres, metal fraction 0.155. The results are shown in Figure 6 along with the spectrum of the equal volume spherical aggregate. It is clear from the figure that, while the ellipsoidal aggregates are slightly more extinctive in the UV than spherical ones and have plasmon bands that are slightly less red-shifted and less broadened, the spectra are remarkably similar. From this we conclude that spherical aggregates provide a reasonable model for extinction calculations of DNA-linked gold nanoparticle aggregates even though the latter presumably assume a variety of shapes.



**Figure 6.** Extinction spectra of DNA-linked gold nanoparticle aggregates in water; orientational averages of spectra of ellipsoidal aggregates. The spectra are similar, indicating that spectra of ensembles of randomly-oriented equivolume ellipsoidal aggregates are aggregate shape independent.

## CONCLUSIONS

We have developed a dynamical effective medium theory for the dielectric permittivity,  $\epsilon_{\text{eff}}$ , of a class of nanoparticle materials composed of inclusions embedded in a dielectric medium. The theory is applicable to systems in which uniformly sized nanoparticles are separated by distances greater than or equal to a particle radius and are exposed to radiation at energies such that the wavelengths are long relative to the nanoparticle size. We have applied the theory to materials composed of DNA-linked gold nanospheres in an aqueous medium. In these materials, interparticle separations are controlled by the number of base pairs in the duplex DNA interconnects and are sizable enough to satisfy the conditions for accuracy of the theory. Using the dynamical EMT dielectric function, we are able to calculate linear optical properties of nanoparticle aggregates of various shapes and sizes using electrodynamic methods appropriate for the specific aggregate shapes.

We have tested the dynamical EMT by comparing aggregate extinction spectra calculated using the derived dielectric function,  $\epsilon_{\text{eff}}$ , with spectra calculated using explicit particle models and accurate electrodynamic methods that are converged with respect to the order of interaction between the particles. By virtue of the indistinguishability of the EMT spectra and spectra calculated using exact methods, we conclude that the homogeneous representation provided by the effective dielectric function is accurate. We have also adopted an electrodynamic computational scheme based upon the DDA<sup>9</sup> for calculating optical properties of arbitrarily

shaped targets and have used it to calculate the extinction spectra of aggregates that are ellipsoidal (oblate and prolate) in shape and have eccentricities as large as 5:1. For these latter calculations we again used the EMT dielectric function.

Spectra were calculated for individual aggregates oriented with respect to the incident light and also for populations of randomly oriented aggregates, such as would be present in the aqueous environment where DNA-directed assembly takes place. The calculations show that, for nanoparticle aggregates that are ellipsoidal in shape and oriented with respect to the polarization and propagation directions of the incident light, the location of the plasmon band is a function of both shape and orientation. However, the spectra calculated for orientationally averaged populations of ellipsoidal aggregates display very little sensitivity to aggregate shape, as long as the aggregate volumes are held constant. From this we conclude that, when calculating extinction for DNA-linked nanoparticle aggregates, one can assume that the aggregates are spherical even though the aggregates formed in the laboratory may assume a variety of shapes.

The spectra displayed here for the purpose of illustrating the accuracy of the dynamical effective medium theory have plasmon bands that are only modestly red-shifted and broadened relative to the plasmon band of dispersed particles. Elsewhere<sup>8</sup> we have shown that the more substantial aggregation-induced spectral changes that are observed experimentally (Fig. 1) can be reproduced in calculated spectra if the nanoparticle aggregate sizes are chosen to be larger than the sizes used here to illustrate the theory.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. R. C. Mucic, J. J. Storhoff, R. L. Letsinger and C. A. Mirkin, *Nature* **382**, 607 (1996).
2. R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, and C. A. Mirkin, *Science* **277**, 1078 (1997).
3. J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin, and R. L. Letsinger, *J. Am. Chem. Soc.* **120**, 1959 (1998).
4. J. J. Storhoff, A. A. Lazarides, C. A. Mirkin, R. L. Letsinger, R. C. Mucic and G. C. Schatz, *J. Am. Chem. Soc.* **122**, 4640 (2000).
5. A. A. Lazarides and G. C. Schatz, *J. Phys. Chem.* **104**, 460-7 (2000).
6. A. A. Lazarides and G. C. Schatz, *J. Chem. Phys.* **112**, 2987 (2000).
7. A. A. Lazarides and G. C. Schatz, *J. Chem. Phys.*, to be submitted.
8. A. A. Lazarides, K. L. Kelly, T. R. Jensen, and G. C. Schatz, *Theochem*, **529**, 59 (2000).
9. B. T. Draine, P. J. Flatau, *J. Opt. Soc. Am. A* **11** 1491 (1994); B.T. Draine, J. J. Goodman, *Astrophys. J.* **405**, 685 (1993); Program DDSCAT, by B. T. Draine, P. J. Flatau. University of California, San Diego, Scripps Institute of Oceanography, 8605 La Jolla Dr., La Jolla, CA 92093.
10. W. H. Yang, G. C. Schatz and R. P. Van Duyne, *J. Chem. Phys.* **103**, 869 (1995); T. Jensen, L. Kelly, A. Lazarides and G. C. Schatz, *J. Cluster Science* **10**, 295 (1999).